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Initial Surface Structure of Flame-Annealed Au(100) in Aqueous

Solution: Consistency between In-Situ Scanning Tunneling

Microscopy and Electrochemical Results

by

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The aim of this note is to clarify the initial superficial structure of gold (100) electrodes following the commonly utilized flame-annealing pretreatment procedure, by using atomic - resolution scanning tunneling microscopy (STM), and to show the consistency of electrochemical and STM results.

Initially in 1974 it was reported that the Au(100) electrode in aqueous electrolyte exhibited some hysteresis in the differential capacity-electrode potential curves and the cyclic voltammograms within the double-layer region [for example, refs 1-4]. This hysteresis depends on the negative potential limit and the potential-time history. In electrolytes exhibiting only slight ionic adsorption at the potential of zero charge (E_{pzc}) such as perchloric acid, the potential of the capacity minimum, E_{min} , arising from the diffuse layer was shown to be shifted in the positive direction following an excursion to more negative potentials [for example, see Fig.2 of ref.3]. These shifts of E_{min} were suggested to be due to increases in E_{pzc} , and to an alteration of the Au(100) surface order, specifically to reconstruction that is induced at negative electrode charges and lifted during the potential sweep only at potentials positive of E_{pzc} [1-4]. Then the phase transition gives rise to a positive current peak denoted C in ref. 3 and shown in fig. 38a of ref. 4. The reconstruction can be restored by returning to potentials sufficiently negative of E_{pzc} .

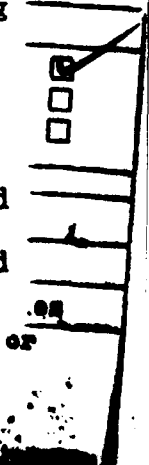
From 1985, Kolb and coworkers have also discussed potential-dependent surface reconstruction of flame-annealed



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Au(100) electrodes, focussing on the behavior of the initial positive-going potential scan in dilute perchloric and sulfuric acids [5-7]. They observed a markedly (0.22V in 0.01 M HClO_4) more positive E_{min} during this initial potential excursion relative to subsequent scans. They interpreted this behavior, along with electron diffraction data for emersed electrodes, as indicating the presence of extensive *initial* reconstruction of the freshly annealed Au(100) surface. The reconstruction was apparently lifted only by sweeping the potential to large positive charges where extensive anion adsorption occurs, and was inferred to return partially by applying sufficiently negative electrode potentials [6]. In contrast, for flame-annealed Au(100), Hamelin observed only a slight (10 mV) shift of E_{min} under these conditions, i.e., between the first and subsequent potential scans, as long as excursions to potentials more than 0.2 V below E_{min} were avoided [3]. The values of E_{min} observed for the first potential scan suggested that an *unreconstructed* [i.e., (1 x 1)] Au(100) surface is present under these conditions, the reconstruction being triggered only upon sweeping to potentials well (≥ 0.2 V) below E_{min} .

Recently we have been able to acquire atomic-resolution surface structural information for ordered gold electrodes in aqueous media by means of in-situ scanning tunneling microscopy (STM) [8-10]. For the Au(100) surface in aqueous perchloric acid, a (5 x 27) reconstruction is observed after altering the potential to values, -0.3 to -0.4 V vs SCE, well below E_{min} (ca

0.05 V vs SCE) [8,11]. In our initial study [8], the freshly annealed surface was first cycled at 50 mV s^{-1} between 0.2 and 1.3 V in order to check the surface state. Subsequent STM images at 0.2 V clearly showed the predominant presence of a (1 x 1) Au(100) surface. Qualitatively concordant in-situ results have also been obtained by Second Harmonic Generation (SHG) [12] and X-Ray diffraction [13].

It is therefore now well established that such Au(100) electrochemical interfaces are reconstructed at negative charges, and not reconstructed at sufficiently positive charges. However, the superficial structure of Au(100) initially following flame treatment remains controversial, the electrochemical results noted above for the first potential scan in dilute perchloric acid being markedly at variance [3,5,6]. As mentioned above, the main purpose of the present Note is to clarify this specific point. Some electrochemical results which support further the new STM observations will also be presented.

For this purpose, then, it is of interest to examine the STM images of freshly annealed surfaces under clean conditions *without prior potential cycling*. The specific question to be addressed here is : what is the Au(100) structure following the conventional surface pretreatment involving flame annealing and cooling in ultrapure water ? Three types of STM experiments were performed to address this issue.

1) The first involved transferring the annealed surface immediately to the STM cell protected by a drop of water and 0.1 M perchloric acid added. The STM images were then obtained under potential control in the region ca -0.1 to 0.2 V vs SCE *without* undertaking prior voltammetric excursions. (See ref. 8 for other procedural details). Atomic-resolution STM images were obtained reproducibly under these conditions which showed the presence of a predominantly *unreconstructed* Au(100) structure. An example of such an image obtained in this manner is shown in Fig. 1A. The characteristic square-planar structure of a (1 x 1) surface is clearly discerned, with an interatomic spacing of 0.29 (\pm 0.02) nm, as expected for gold. Imaging different surface regions, including domains up to ca 50 nm square, yielded persistently a (1 x 1) structure. These images are essentially identical to those obtained (as reported in ref. 8) at 0.2 V vs SCE for surfaces for which one or more prior potential cycles from 0 to 1.3 V were performed .

2) Similar STM images were obtained *in air* immediately following flame annealing and cooling in ultrapure water. This finding indicates that the reconstruction is essentially absent even prior to immersing the surface in aqueous perchloric acid under potential control.

3) For surfaces that underwent flame annealing and subsequent cooling *in air* rather than in ultrapure water, the STM images, obtained *in air*, exhibited reconstruction of portions of the Au(100) face, yielding (5 x 27) domains.

All this infers that the presence of clean water during the cooling step after clean annealing prevents reconstruction; (3) is consistent with the reconstruction of clean Au(100) observed in ultrahigh vacuum (UHV) following surface annealing [14].

After obtaining STM images such as that shown in Fig. 1A, altering the potential to more negative values, below -0.2 V vs SCE, yielded the progressive formation of (5 x 27) reconstructed domains over a 5-10 min period. A typical image of this type, obtained at -0.3 V, is shown in Fig. 1B. (The nature of this surface structure is detailed in refs 8 and 11). After returning to 0.2 V for several minutes, the reconstruction is seen to be largely lifted, predominantly (1 x 1) domains being recovered (cf ref.8). This reversible potential-dependent reconstruction as observed by STM is in broad agreement with the structural information obtained from in-situ surface X-Ray diffraction data [13], as well as being in harmony with the new electrochemical results given below.

The present STM results therefore confirm the original interpretation of potential-induced reconstruction for Au(100) put forward by Hamelin on the basis of electrochemical data [2,3]. Most importantly, it is now clear that a *freshly flame-annealed* Au(100) surface cooled in ultrapure water is initially *unreconstructed* both before and after immersion in perchloric acid electrolyte at potentials close to E_{\min} . As suggested in ref. 3, reconstruction at this clean surface is

subsequently induced only by altering the potential to values below E_{\min} .

Prompted by the STM findings, additional capacitance-potential, $C(E)$, curves were obtained for Au(100) in dilute (0.01 M) perchloric acid in the following way. Following surface annealing and cooling in pure water, the gold face was put in contact with the solution at - 0.05 V, and the positive-going $C(E)$ curve up to 0.6 V and then the negative-going curve were recorded (fig.2 a). Similar results were already described in ref.3. The limits for the potential cycles were then set at - 0.4 and 1.4 V, and the potential was held at - 0.35 V vs SCE for progressively longer times (0, 2, 4, and 6 minutes). The $C(E)$ curves for the positive-going potential scans were recorded just after each holding period. The resulting $C(E)$ traces, labelled as such, are shown in fig.2 b, together with the corresponding (and invariant) following negative-going $C(E)$ trace (dotted curve). While the latter curve clearly shows the usual diffuse-layer minimum at 0.05 V vs SCE, identified with E_{pzc} , the former curves display deviations that increase progressively with longer hold times at -0.35 V. Interestingly, the capacitance minimum becomes noticeably shallower and broader, as well as E_{\min} shifting positive under these conditions. If then the negative-going exploration is limited at - 0.1 V, the positive-going trace is similar to the negative one (fig.2 c), the time period being not long enough to produce noticeable reconstruction.

The $C(E)$ changes seen in fig.2 b are consistent with the progressive reconstruction which is known from STM to occur under these conditions. While the (1×1) structure, formed by prior potential excursion to positive values, yields a sharp $C(E)$ minimum corresponding closely to E_{pzc} , the increasingly reconstructed surfaces exhibit less and less clearcut minima. The latter arise from the nonuniformity of the electronic charge on the (5×27) corrugated surface and on reconstructed domains of nonuniform sizes and longer-range structure, as deduced by STM [11]. In this regard, then, the situation is somewhat akin to that of polycrystalline surfaces of high melting metals, which yield similarly broad and ill-defined $C(E)$ minima [15, 16]. Further analysis of $C(E)$ data for reconstructed gold surfaces would be of particular interest with regard to unraveling the spatial variations in surface electronic charge density.

It should be stressed that the reproducible acquisition of such electrochemical data requires careful attention to cleanliness. Under such conditions, one of us (AH) has performed numerous (specifically 77) observations of the first and subsequent potential scans following transfer of freshly annealed Au(100) to either aqueous perchloric or sulfuric acid [3]. The lack of significant hysteresis in perchloric acid between these scans (provided that potential excursions beyond 0.2 V negative of E_{min} are avoided) (fig.2 a and c) is reproducibly obtained. Capacitance curves similar to the results of Kolb et al [5-7], featuring a large hysteresis between the first and subsequent scans, could occasionally be obtained in perchloric acid, but

only when less attention was paid to cleanliness of the cooling procedure and the electrolyte solutions.

The deduction of Kolb et al that flame-annealed Au(100) surfaces are initially reconstructed was based in part on electron-diffraction measurements following subsequent transfer to UHV [6]. While we have no reason to question the latter observation, in contrast to the former interpretation the present *in-situ* STM data show that such reconstruction is initially absent in the electrochemical cell when the annealing and water cooling-step are carefully controlled. Given that clean Au(100) surfaces in UHV are reconstructed at room temperature, it appears that the water-cooling step in the flame-annealing method used commonly for electrochemical studies may play a key rôle in preventing reconstruction. This is consistent with our STM observation that Au(100) remains unreconstructed at equilibrium at E_{pzc} in aqueous perchloric acid, where anion adsorption is largely absent and the surface is uncharged. The reconstruction on Au(100) is apparently triggered by the presence of negative surface electronic charge densities [8].

We have demonstrated the consistency of STM observations and C(E) curves for Au(100), but we have also noted the extreme sensitivity of Au(100) surface structure to the experimental procedures followed.

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FIGURES CAPTIONS

Fig.1 - Atomic -resolution STM images obtained with Au(100) in 0.1 M perchloric acid.

(A) Unfiltered image observed just after flame annealing and cooling in pure water; at - 0.1 V vs SCE, showing the (1x1) structure. Tunneling conditions : constant current mode, $i_t = 25$ nA, bias voltage $V_b = 10$ mV.

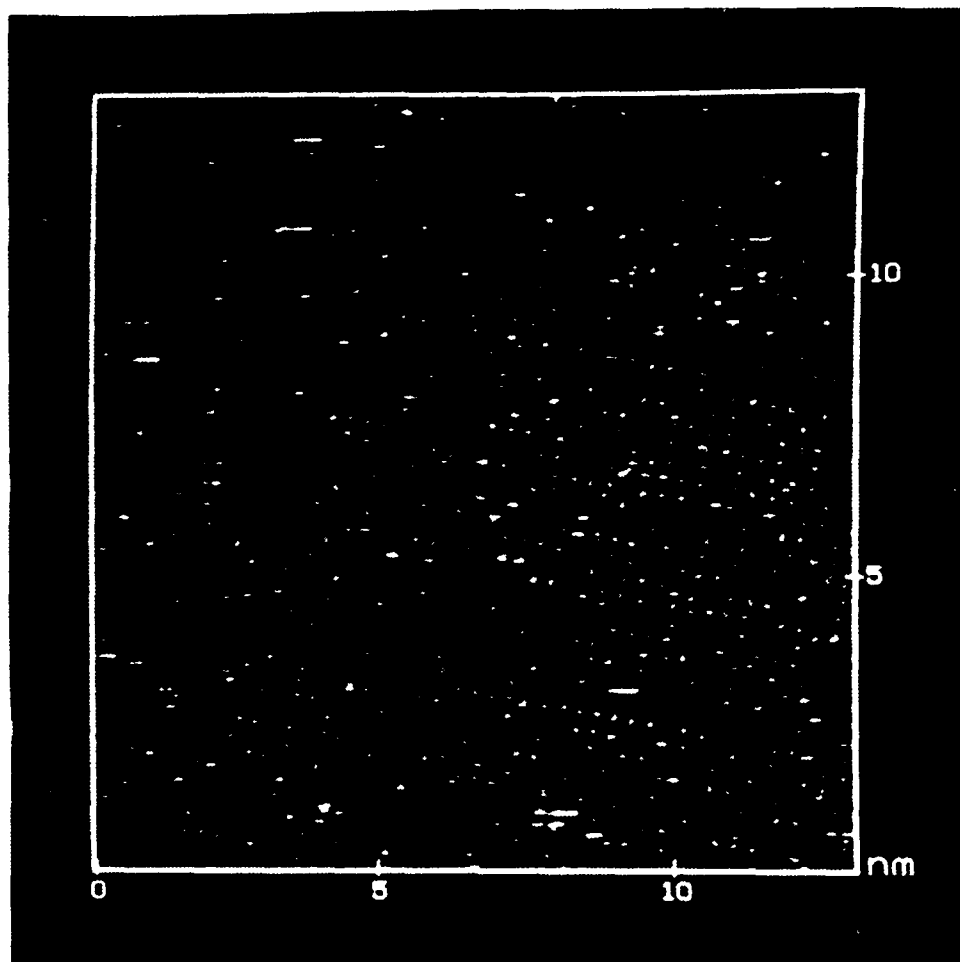
(B) Height-shaded image (taken 30° from surface normal) at - 0.3 V vs SCE showing the reconstructed structure discussed in refs. 8 and 11 ; $i_t = 20$ nA, $V_b = 12$ mV.

Fig.2 - Differential capacity- potential curves for Au(100) in 0.01 M perchloric acid (20 Hz, 8 mV/s).

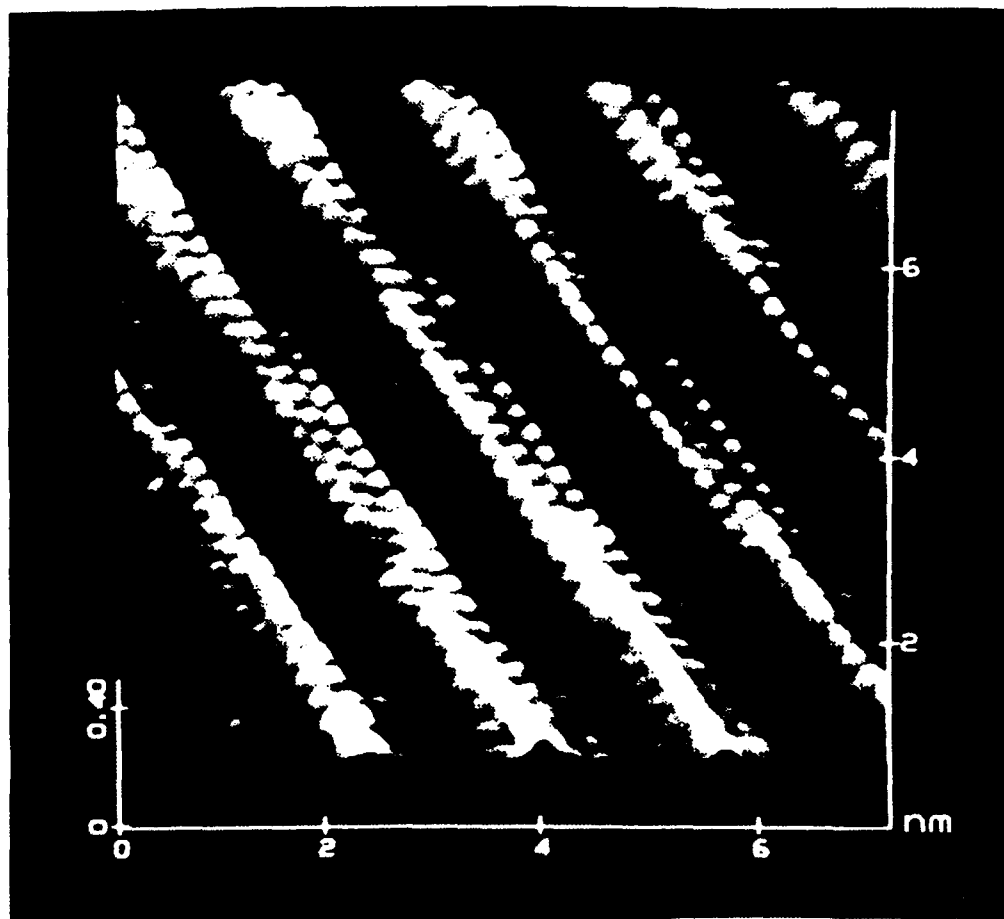
a) Positive-going and then negative-going C(E) curves observed just after contact of the electrode with the solution at -0.05 V ;

b) (.....) negative-going C(E) curves observed after oxidation and reduction of the gold surface following the four positive-going curves shown in the Figure, obtained after holding the potential at - 0.35 V for (——) 0, (- - -) 2, (- . - .) 4, (- ... -) 6 minutes (as indicated) ;

c) (.....) negative-going C(E) curve and (——) positive-going curve for a negative limit of - 0.1 V vs SCE.



A



B

